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PROGRESS REPORT NO. 26

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I. SURFACE STUDIES

A. SURFACE THEORY

The reflectivity equations given in last month's report were reformulated in order to provide faster convergence of the computations. For large barrier thicknesses, an asymptotic expansion of the confluent hypergeometric function of the second kind can be used.[1] This expansion provides a series expression which converges much more rapidly than the exact expression. For large barrier widths, asymptotic expansions for these solutions are available.

B. SURFACE CHARACTERIZATION CHAMBER

Samples from several surface characterization experiments underwent chemical surface analysis by Auger spectroscopy. Results are given in pertinent sections of this report. A spray coating of LaB_6 on a tantalum support was held at 1273 K for two minutes in the Surface Characterization Chamber. This heat treatment resulted in the elimination of boron oxide and a slight reduction of oxygen and carbon.

Modifications were made to the Surface Characterization Chamber. The sputter ion gun was moved to a side port to permit normal incidence sputtering. The elemental cesium source was replaced with an array of cesium channels.

C. ACTIVATION CHAMBER EXPERIMENTS

Earlier results were confirmed indicating that work functions in the 1.0 to 1.1 eV range can be obtained with alternating exposure of LaB_6 surfaces to cesium and oxygen. Identical results were observed with both sintered and sprayed LaB_6 (supplied by CERAC). Moreover, no difference was observed between spray coatings on nickel and on tantalum.

During August the primary emphasis was placed on measuring bare work functions of different LaB_6 surfaces because preliminary experiments indicated that there are large differences. Four types of surfaces were studied: 1) sintered LaB_6, 2) sprayed LaB_6 on a cathode nickel substrate*, 3) sprayed LaB_6 on a tantalum substrate (this substrate was chosen because it allows heat cleaning to the temperature at which oxygen is removed) and 4) single crystal LaB_6, bonded to nickel and to tantalum.

The results are summarized in Table I-1. As was reported previously, sprayed LaB_6 on cathode nickel has a lower bare work function than sintered material. This could possibly be attributed to the absence of contaminants known to be contained in the surface of sintered material. However, the bare work function of the spray coating on tantalum was found to be similar to that of sintered LaB_6, indicating an unexplainable effect of the substrate material on the LaB_6 work function. Comparison of spray coatings on nickel and on tantalum by SEM did not show any significant difference.

To gain more information on the bare work function of LaB_6, experiments were made with single crystals of LaB_6. The samples were small chips of about 4 mm^2 area, grown and supplied by Dr. G. H. Olsen of RCA Laboratories in Princeton, N. J. These crystals were bonded with AQUADAG (colloidal graphite) to cathode nickel and tantalum substrates. The results were similar to those obtained with spray coatings (i.e., work functions as low as 2.11 eV at 900 K on cathode nickel and above 3 eV on tantalum). Moreover, the work function on cathode nickel was temperature dependent, again similar to the measurements made with the spray coatings on nickel.

*Cathode nickel refers to the substrate material used by RCA to produce their BaO cathodes.

TABLE I-1

WORK FUNCTION OF LaB_6 AT 900 K

Material	Sample #	ϕ(eV)
Sintered	33	> 3
	34	> 3
	35	> 3
	216	> 3
Sprayed on Nickel	38	2.23
	80	2.57
	222	2.22
	223	2.00
	227	2.40
	228	2.62
	229	2.17
	233	2.12
Sprayed on Tantalum	225	> 3
	230	> 3
	234	> 3
Single Crystal (bonded to Nickel)	231	2.15
	235	2.11
Single Crystal (bonded to Tantalum)	238	> 3

The discrepancy between these measured low work functions on cathode nickel substrate and the higher published values for single crystal LaB_6 raised the question of whether the emission had originated from the uncoated sidewalls of the substrate cathode nickel cylinder. This possibility had not been considered before because nickel is known to have a work function above 4 eV; therefore, any thermionic emission from the cylindrical surface should be negligible. Consequently a control experiment was made with an uncoated cathode nickel substrate. The result was a surprisingly low work function of 1.96 eV at 900 K, indicating that the low values obtained with LaB_6 were due to the sidewalls of the substrate. However, in these experiments cesium-oxygen alternation did not produce the low work functions obtained with all sintered and sprayed LaB_6 samples. The work function was at least 0.5 eV higher.

At his time the exceptionally low work function of the cathode nickel substrate is not understood. Because such low work function uncesiated metallic surfaces are of great interest, analyses of this effect are con[illegible]ing.

II. PLASMA STUDIES

A. CONVERTER THEORY

No work was performed on this task during this reporting period.

B. ENHANCED MODE CONVERSION EXPERIMENTS

In order to determine the mechanism which prevents laser-polished nickel mirrors from being spaced at less than 0.1 mil (25 μm), SEM observations were made of the mirror surfaces. Apparent dust particles, sufficiently large (0.8 mils or 20 μm) to account for the threshold spacings, were seen on surfaces which had been exposed to air. This conclusion was reinforced by capacitance measurements made with laser-mirror surfaces placed on a dust-free laminar flow bench which indicated that two such surfaces would contact each other (metal-to-metal) only after they had been carefully cleaned with a stream of dry nitrogen.

A capacitive sandwich structure consisting of two laser-polished nickel mirrors separated by a light dusting of 0.05 μm alumina particles (Linde B) maintained a constant interelectrode spacing of 0.2 mils (5 μm) while the "emitter" electrode was temperature cycled between room temperature and 1173 K. Apparent "shorting" of the electrodes was prevented by biasing one of the electrodes plus or minus 6 V with respect to the other one. These investigations have been interrupted due to a malfunction in the vector impedance meter.

III. CONVERTER DEVELOPMENT

A. LOW-TEMPERATURE CONVERSION EXPERIMENTS

1. Tungsten Emitter, Nickel Collector (Converter No. 177).

In an effort to introduce oxygen into a converter, cesium carbonate powder was substituted for cesium in the reservoir of a standard variable spacing diode. This diode employed an electro-polished tungsten emitter and a nickel collector. The reservoir, made of nickel, was capable of being heated to above 873 K, the decomposition temperature of cesium carbonate. At this temperature cesium carbonate decomposes to form elemental cesium and cesium peroxide (Cs_2O_2) while releasing gaseous carbon dioxide[2]. The diode was processed so that the carbon dioxide would be pumped out of the converter prior to testing.

Collector work function values around 1.3 eV were calculated from the I-V characteristics (dc back-emission). These characteristics were severely spacing and voltage dependent. Emitter work functions obtained from the same I-V curves ranged from 1.4 eV at 700 K to 2.9 eV at 1450 K depending on the relative temperatures of the plumbing, diode flanges and reservoir. The most sensitive parameter was the bellows temperature of the converter. Apparently, most of the cesium had condensed there. Output characteristics taken at stable converter temperatures showed a diminishing cesium effect with time. To recover the cesium, the entire diode, plumbing, and reservoir were heated to above 973 K. This liberated some cesium as noted from the emitter saturation currents. However emitter work functions remained around 3 eV at 1400 K. During the entire test-life no indication of diode

ignition was observed, implying that the cesium pressure must have remained below .05 torr. This, together with the high work function values, indicated the diode was operated under cesium starved conditions. Such low cesium pressures may be due to a reverse reaction below 873 K whereby cesium and cesium peroxide combine to form Cs_2O. If this is the case, all parts of the device must be maintained above 873 K. During an attempt to reheat above this temperature, electrical shorting of the diode terminated these experiments.

B. HIGH EFFICIENCY CONVERSION EXPERIMENTS

1. Tungsten Emitter, Lanthanum Hexaboride Collector (Converter No. 166).

Oxygen was introduced into this converter by diffusion through a 0.37 mm thick layer of LaB_6 bonded to the "showerhead" collector. This addition of oxygen lowered the collector work function to a minimum value of 1.2 eV at a T_C of 550 K as measured by back emission.

After initial reduction of the work function with cesium to 1.35 eV, oxygen was introduced into the converter with the collector at 600 K, the emitter at 550 K, and the cesium reservoir at 300 K. With one torr of oxygen pressure behind the showerhead, diffusion through the LaB_6 was immediate and the collector work function rapidly increased to a value greater than 2.0 eV. The cesium pressure was then increased until the collector work function was again lowered to a minimum value of 1.25 eV at a T_C/T_R of approximately 1.65. Only one alternation of cesium and oxygen was necessary at T_C = 600 K to reach this minimum work function. Additional doses of oxygen produced no improvement. At a reduced collector temperature of 550 K, two alternations of oxygen and cesium lowered the work function to

eV, the lowest value measured in the converter.

Oxygen was also introduced into the converter during operation in the ignited mode. The conditions were T_R = 1400 K, T_C = 850 K T_R = 577 K and d = 2.5 mm. The addition of oxygen increased the emitter saturation current by a factor of two. Testing of this converter will continue.

IV. COMPONENT HARDWARE PROGRAM

A. HOT SHELL DEVELOPMENT

A 0.225 mm tungsten coating was deposited on the inside surface of a hollow shell of POCO PLC-1 graphite. Appearance and thickness were quite uniform. The graphite-tungsten composite shell was tested by means of a helium-mass spectrometer leak detector.

Minor modifications were made to the 10 N KOH scrubber, described in last month's report, in order to prevent flow restrictions due to tungsten oxide formation in the scrubber exhaust.

A literature survey was conducted of techniques for metallizing and brazing to ceramics, in particular to silicon carbide. Present work on this subject is best summarized in Reference 3.

A considerable amount of work on the brazing of metals to graphite and alumina has been conducted at Oak Ridge National Laboratory (ORNL).[4,5,6] Brazing to silicon carbide was discussed by telephone with D. A Canonico of ORNL. He was of the opinion that the same brazes used for graphite should wet silicon carbide. Similar discussions were held with Dr. Walter H. Kohl. He agreed that the methods and braze materials applicable to graphite should be applicable to silicon carbide.

There are, according to Dr. Kohl, two commercially available brazing alloys having the ability to wet and braze carbides: 1) Ticusil®, a 4.5% Ti, 26.7% Ca, 68.8% Ag alloy having a brazing range of

1100 - 1120 K, available from Western Gold and Platinum Company of Belmont, California; and 2) Braze 852, a 85% Ag, 15% Mn alloy having a brazing range of 1230 - 1240 K, available from Handy & Harman of New York, N.Y. Literature about these brazes has been obtained from their respective manufacturers. The usefulness of both of these brazes in bonding silicon carbide hot shell thermionic converters is somewhat doubtful, however, because of their high silver content.

Dr. Kohl reported that cobalt-nickel and platinum-palladium brazes for silicon carbide have been mentioned in literature reviews published by Battelle Memorial Institute. An article published in Le Vide, 1975, by Schneider of Czechoslovakia describes a rhodium-zirconium brazing alloy. A Consultants Bureau translation, published in 1970, of a group of Russian articles about silicon carbide discussed brazes using this material.

Simulated furnace testing continued at a furnace gas temperature of 1573 K (2370 F). The inside of the shells is evacuated to 10^{-7} torr. Table IV-1 presents the status of these tests as of September 6, 1977.

TABLE IV-1

SIMULATED FURNACE TESTS

(6 Sept. 1977)

HOT SHELL	TEST HOURS	COMMENT	DATE OF TEST INITIATION
REACTION BONDED SILICON CARBIDE	13,325	LEAKTIGHT THIS HOT SHELL WAS BRAZED TO A MOLYBDENUM SLEEVE WITH NICKEL-COPPER	9 April 75
KANTHAL A1	11,738	LEAKTIGHT	25 Aug. 75
KANTHAL A1	11,604	LEAKTIGHT	9 Sept. 75
INCONEL 671	4,775	LEAKTIGHT	17 Nov. 76
CHROMIZED STAINLESS STEEL 446	4,775	LEAKTIGHT	17 Nov. 76
KANTHAL A1	1,922	LEAKTIGHT	7 May 77

REFERENCES

1. M. Abramowitz and F. Stegan, Handbook of Mathematical Functions, Dover Publications, Inc., New York (1965).

2. T. R. Briere and A. H. Sommer, J. Applied Phys. 48, 3547 (1977).

3. W. H. Kohl, Handbook of Materials and Techniques for Vacuum Devices, Reinhold Publishing Corp., New York (1967).

4. D. A. Canonico, N. C. Cole, and G. M. Slaughter, "Direct Brazing of Ceramics, Graphite, and Refractory Metals", ORNL/TM-S195, Contract No. W-7405 - eng-26, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

5. J. P. Hammond and G. M. Slaughter, Welding Journal, 50, 33 (1971).

6. R. G. Donnelly and G. M. Slaughter, Welding Journal, 41, 461 (1962).

HOT SHELL MATERIALS
TECHNOLOGY IN SUPPORT OF
ADVANCED THERMIONIC TECHNOLOGY

CONTRACT: 7070-4190-411 Mod. #3

PROGRESS REPORT NO. 6

REPORTING PERIOD: 1 August through 31 August 1977

PREPARED FOR:

THERMO ELECTRON CORPORATION
101 First Avenue
Waltham, Massachusetts, 02154

Dated: 7 September 1977

TRW
SYSTEMS GROUP

1.0 INTRODUCTION

This report describes the progress under contract 7070-4190-411 Mod. #3 during the period of 1 August through 31 August 1977. It is submitted as a contract deliverable summarizing the monthly technical effort.

2.0 PROGRAM OBJECTIVES AND TASKS

The objective of this program is to develop, select and evaluate candidate alloys or alloy/coating combinations as protective cover materials for thermionic devices operating as energy converters (topping cycles) in the fossil fuel combustion product environment of steam power plants.

The program has the following tasks:

- o Development of surface alloying process and evaluation of surface alloyed materials in sulfidizing-oxidizing environments of 2200-2400°F.
- o Performance of long-term and thermal cyclic tests to determine the chemical-metallurgical stability of promising materials.
- o Investigation of fabrication process for producing hot shell shapes and fabrication of hot shell samples based on technical and economic merits as deliverables to Thermo Electron for testing.

3.0 TECHNICAL PROGRASS

During the past month, three (3) 100-hour 2200°F hot corrosion test runs and one 2200°F thermal cycle test run (four 100-hour cycles) were completed. A second thermal cycle run and a long-term isothermal hot corrosion test run were initiated.

The three hot corrosion test runs #5, #6 and #7 consist of the following specimens: Run #5(9 specimens) INCO 671,INCO 690,PAS Cr_2O_3 coated 309,PAS Cr_2O_3 coated HC, PAS Cr_2O_3 coated 446, PAS Cr_2O_3 coated 1018 steel, electroplated (Cr/Ni/Cr/Ni/Cr) 446, chromized 446 and chromized 1018 steel.

Run # 6 (8 specimens): INCO 671, INCO 690, electroplated (Cr/Ni/Cr/Ni/Cr) 446, PAS Nichrome on 446, PAS 50Ni/50Cr alloy on 446, PAS 50Ni/50Cr alloy on HC, PAS 50Ni/50Cr alloy on 309, PAS 50Ni/50Cr alloy on 1018 steel.

Run #7 (4 specimens): INCO 671, INCO 690, electroplated and diffusion treated Cr/Ni/Cr/Ni/Cr on 309, electroplated and diffusion treated Cr/Ni/Cr/Ni/Cr on 1018 steel.

Results of Runs #5,#6 and #7 indicated that INCO 671, INCO 690 and PAS Cr_2O_3 on 446 and HC look very good. Others failed due either to chemical reaction and/or coating delaminations.

Based on these results the second thermal cycle run and a long-term (2000-hour) hot corrosion run were initiated to include the following specimens:

- Thermal cycle Run #2: INCO 671, INCO 690, PAS Cr_2O_3 coated 446, PAS Cr_2O_3 coated 309, PAS Nichrome and diffusion treated HC, electroplated Cr/Ni/Cr/Ni/Cr and diffusion treated 309
- Long-Term Corrosion Test: CVD SiC, REFEL, PAS Cr_2O_3 on 446, PAS Cr_2O_3 on 309, PAS Nichrome on HC.

Metallographic, electron-microprobe and X-ray diffusion analysis of promising and selected test specimens is in progress. A 446 stainless steel tube specimen is being fabricated and will be used as substrate for the most promising coating (to be selected) by either plasma arc spray or by electroplating. The finished specimen will be submitted as a deliverable to Thermo Electron.

Also in progress is the preparation of a summary report on the current program. A program review is tentatively planned for the last week of September at Thermo Electron to discuss technical accomplishments to-date and follow-on efforts.

A. TOY
TRW PROGRAM MANAGER